Journées Plénières du GDR Plasmonique Active

Marseille 10-12 Juillet 2023

cnrs GDR Groupement de recherche
Plasmonique Active

Aix*Marseille université
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INSTITUT FRESNEL

Scientific days of the Active Plasmonics GDR - Marseille July 10-12th

Day 1 Monday July 10th

14:45 *Registration desk opening*

15:30 Welcome introduction words by GDR – Nordin Felidj and Marc Lamy de la Chapelle

15:35 Organization and logistics - Jérome Wenger

15:40 **Plenary talk: Beniamino Sciacca, CINaM, Marseille**
Bottom-up plasmonic metasurfaces à la carte

16:15 **Wajdi Chaabani**, ITODYS, Paris
Self-Assembly of Anisotropic Plasmonic Nanoparticles in Confinement

16:35 **David Grosso**, CINaM, Marseille
Direct NIL patterning of sol-gel based metal oxides, with controlled refractive index from 1.2 to 2.7; applications in optics, photonics, and sensing

16:55 **Pascal Cheng**, ITODYS, Paris
Aluminum metasurfaces with high quality factors and spectral tunability

17:15 *Short Break*

17:30 **AfterConf event #1 Fresnel-Arago historical experiment live demo**

18:00 End

Day 2 Tuesday July 11th

8:45 *Registration desk opening*

9:15 **Plenary talk: Eric LeMoal, ISMO, Univ. Paris Saclay**
Plasmonics and nanophotonics with inelastic tunneling electrons

9:50 **Julien Gabelli**, LPS, Orsay
Role of optical rectification in photon-assisted tunneling current

10:10 **Ali Dabbous**, PPSM, Gif sur Yvette
Plasmon-mediated photoelectrochemical transformations of tetrazine derivatives followed by Fluorescence microscopy coupled with Scanning Electrochemical Microscopy

10:30 *Coffee Break*

11:05 **Sebastien Bidault**, Institut Langevin, Paris
DNA nanotechnology as a playground for plasmonics

11:25 **Prithu Roy**, Institut Fresnel, Marseille
Ultraviolet Resonant Nanogap Antennas from Rhodium Nanocubes for Enhancing Protein Intrinsic fluorescence

11:45 **Aicha Azziz**, IMMM, Le Mans
Observation of DNA strand interaction with SERS

12:05 **Peeranuch Poungsripong**, CINaM, Marseille
Gap-plasmon crystallography

12:25 *Lunch break*

13:30 **AfterConf event #2 Round table discussion: soft skills in and outside science**
Topics to be defined: Carreer management / Stress management / Interpersonnal communication / ChatGPT

14:00 *Mini break restart*

14:10 **Plenary talk: Guillaume Baffou, Institut Fresnel, Marseille**
Optical wavefront microscopy in nanophotonics and thermoplasmonics

14:45 **Celia Arib**, IMMM, Le Mans
Study of thermoplasmonic properties of AuNPs in visible and near infrared region

15:05 **Jean-François Bryche**, LN2, Sherbrooke
Heat Transfer inside Cross-shaped Nanoparticles

15:25 *Coffee Break*

16:00 **Ekaterina Podlesnaia**, IPHT, Jena
Optimizing the synthesis of gold nanotriangles and evaluating their potential in LSPR sensing

16:20 **Qiqian Liu**, IMMM, Le Mans
The Presence of Uncoated Nanoparticle Aggregates Determine the Phase of Phosphatidylcholine Lipids as Evidenced by Vibrational Spectroscopies

16:40 **Kartikey Pandey**, ITODYS, Paris
Surface Lattice modes for biosensing

17:00 **Benjamin Demirdjian**, CINaM, Marseille
FDTD calculations: a crucial tool to predict and interpret LSPR experimental results

17:20 *Short Break*

17:35 **AfterConf event #3 Effective communication for scientists: tips & tricks**

18:20 End

Day 3 Wednesday July 12th

9:15 **Plenary talk: Anne-Laure Baudrion, UTT, Troyes**
Nonlinear optical sensing in arrays of plasmonic nanoparticles

9:50 **Sarra Gam**, ITODYS, Paris
Molecular Imprinted polymer on plasmonic surfaces

10:10 **Jean-François Bryche**, LN2, Sherbrooke
Spatially-Localized Functionalization on Nanostructured Surfaces for Enhanced Plasmonic Sensing Efficacy

10:30 *Coffee Break*

11:05 **Igor Ozerov**, CINaM, Marseille
Fabrication of plasmonic metasurfaces for fluorescence nanoscopy

11:25 **Quanbo Jiang**, UTT, Troyes
Go beyond the limitations for trapping objects from micro to nanosize

11:45 **Jerome Wenger**, Institut Fresnel, Marseille
Improving single molecule fluorescence detection with zero-mode waveguide nanoapertures

12:05 **Scientific round table discussion:** perspectives and prospectives for active plasmonics

12:35 Concluding words by GdR

12:40 End

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GdR Plasmonique Active Scientific Days – Access & Logistics

10th – 12th July 2023

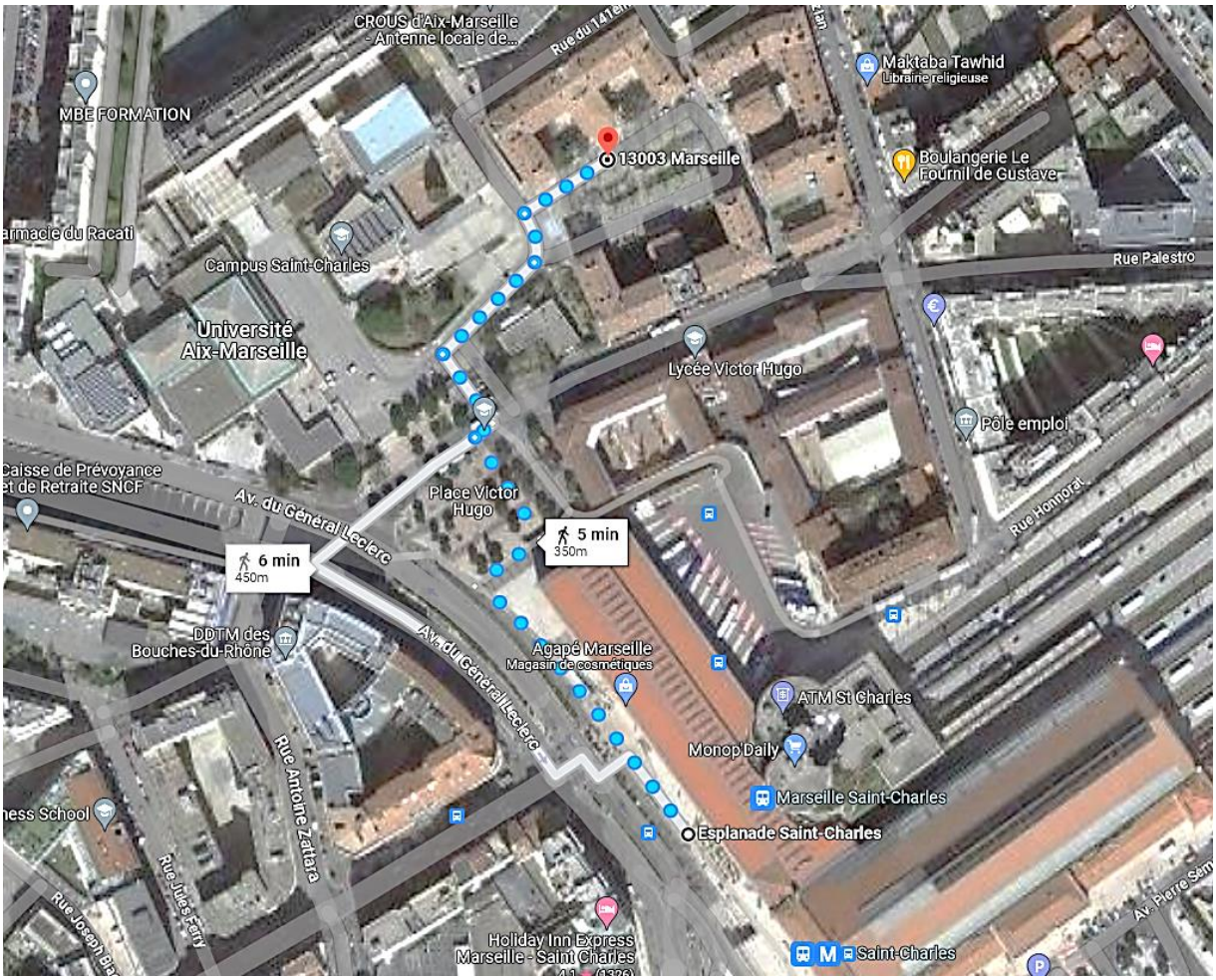
Conference location: Amphithéâtre Sciences Naturelles (building 08)

Marseille Campus Saint Charles

3 place Victor Hugo, Marseille

Access: from outside the train station, take to your right, cross the Victor Hugo place, enter the campus via the gate, show your invitation letter to the guard (who has the list of registered participants), then go to your right to the place with the old amphitheaters, the conference building is on the left, N°08 "Sciences Naturelles" engraved on the top front of the building.

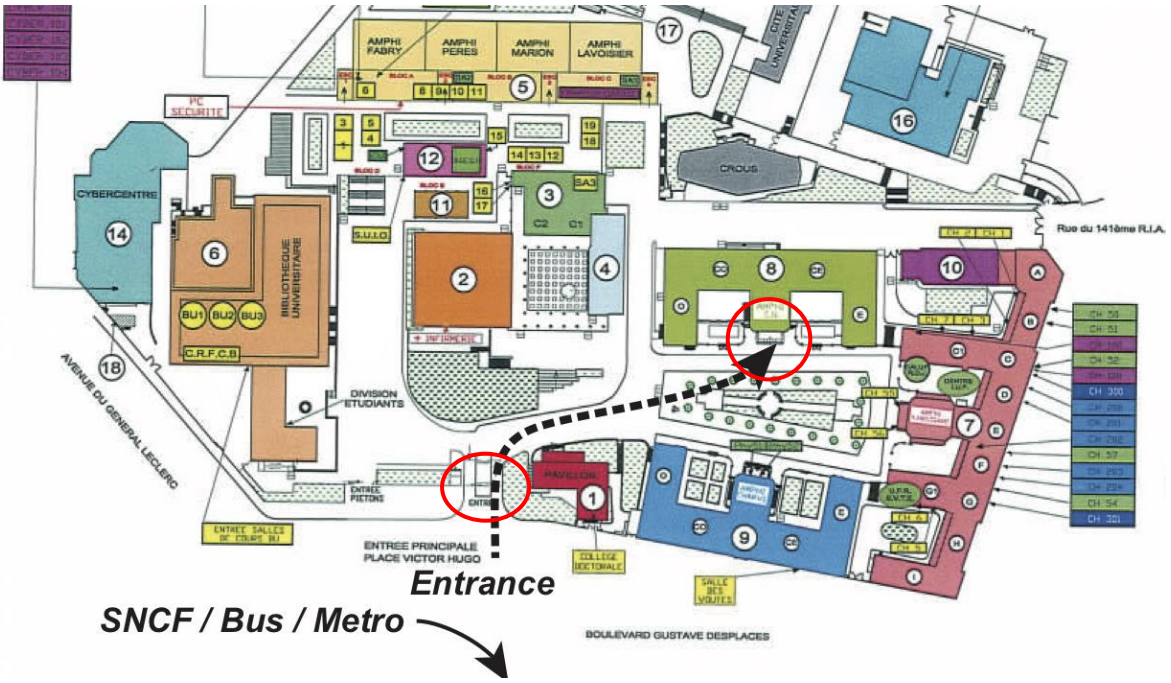
Contact in case of need: Jerome Wenger +33 (0)7 86 39 18 49



New entrance gate at campus

Amphi Sciences Naturelles : conference hall building 8

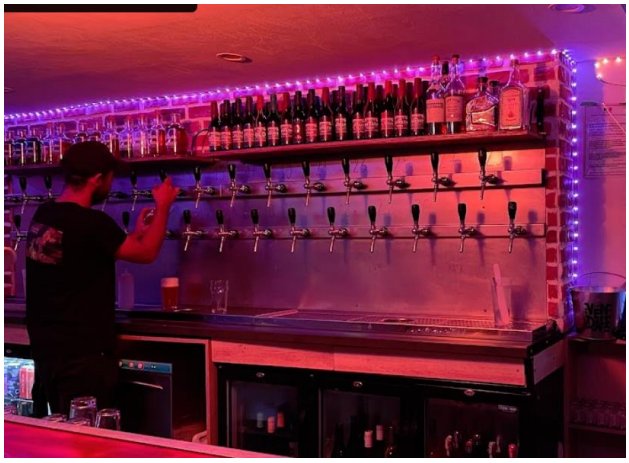
Campus map :



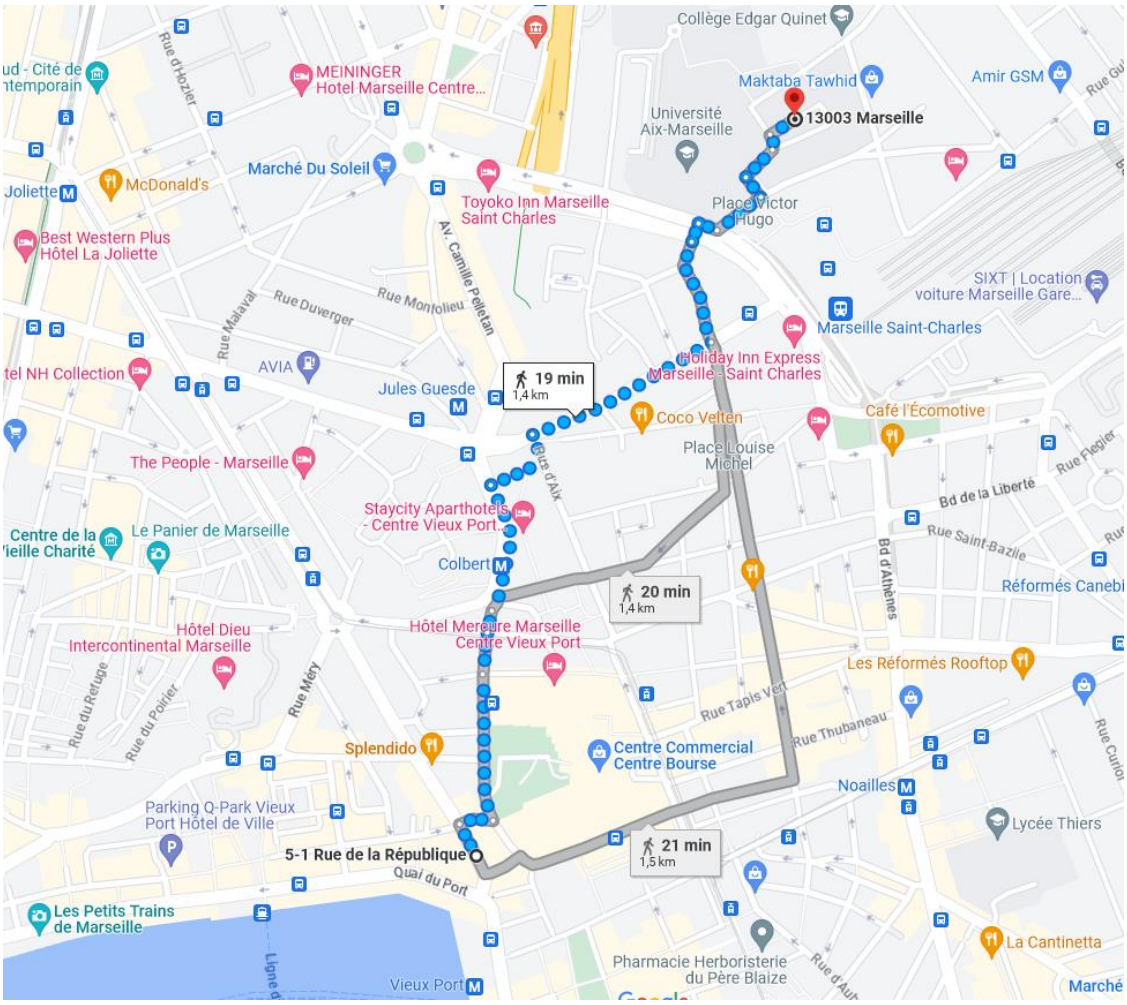
Monday July 10th evening around 9pm

We invite you to join an afterwork session with free drinks and finger snacks at the bar “Beer District” very next to Vieux Port. Don’t forget to bring your badge to unlock your free drinks!

Beer District Marseille 4 rue de la République 13001 Marseille 04 96 22 04 65



To go to Vieux port : from the Saint Charles campus it takes about 20 min walk or take metro line 1 direction La Fourragère and exit at “Vieux Port” station (2 stops)



Plenary speakers

- **Anne-Laure Baudrion** (UTT, Troyes)

  Nonlinear optical sensing in arrays of plasmonic nanoparticles

- **Eric Le Moal** (ISMO, Univ. Paris Saclay)

  Plasmonics and nanophotonics with inelastic tunneling electrons

- **Beniamino Sciacca** (CINaM, Marseille)

  Bottom-up plasmonic metasurfaces à la carte

- **Guillaume Baffou** (Institut Fresnel, Marseille)

  Optical wavefront microscopy in nanophotonics and thermoplasmonics

Self-Assembly of Anisotropic Plasmonic Nanoparticles in Confinement

Wajdi Chaâbani et al.

ITODYS, Université Paris-Cité

Laboratoire de Physique des Solides (LPS), Université Paris Saclay

Three-dimensional (3D) supercrystals (SCs) of plasmonic nanoparticles are a novel class of materials with exciting applications in technologies such as light harvesting or metamaterials. However, their realization relies on extraordinarily regular colloidal building blocks and accurate self-assembly methods. We present here the 3D assemblies in confinement anisotropic gold nanoparticles (e.g. bipyramids) in different mold shapes prepared by soft-lithography [1]. Then, the SCs are characterized by small-angle X-ray scattering (SAXS), scanning electron microscopy (SEM), and optical microscopy.

We demonstrate here that the polygonal mold edge directs the orientation and number domains in the SCs. In addition, by combined SAXS and SEM analysis, we have concluded that the number of domains (n) is correlated with the mold edge number (k). We conclude that n=k/2 when k is pair and n=2k when k is odd. For instance, in Figure 1, we show a triangular SCs shape (k=3) presenting three domains and six Bragg spots (n=6).

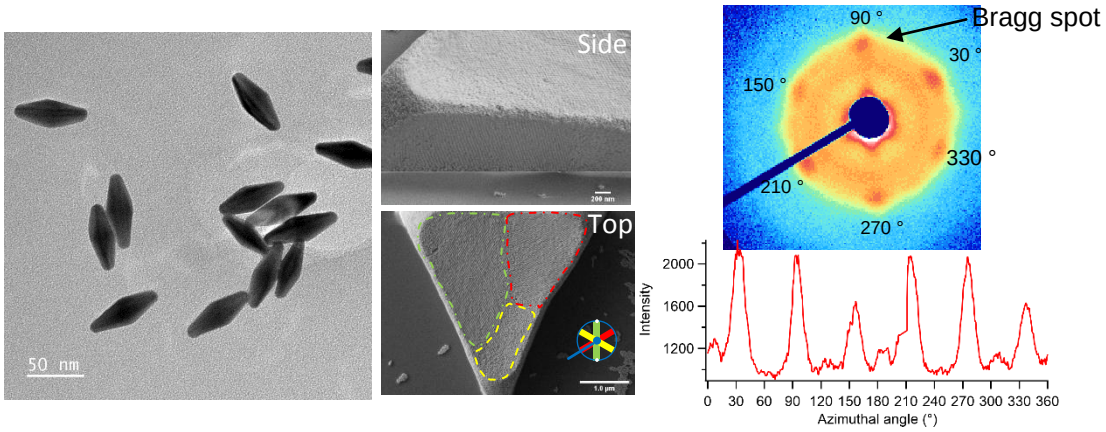


Figure 1: Self-assembly of bipyramids NPs in triangular mold. (left) TEM image, (middle) SEM images of NPs assemblies in triangular mold (top and side views), (right) 2D- SAXS image and azimuthal integration

[1] *C. Hamon et al*. ACS Nano 8 (2014) 10694-10703

Direct NIL patterning of sol-gel based metal oxides, with controlled refractive index from 1.2 to 2.7; applications in optics, photonics, and sensing.

Marco. Abbarchi,[2] Mehrnaz Modaresialam [2], Martin. O'Byrne,[1] Badre Kerzabi [2], Zeinab. Chehadi,[1] Ye. Zhou,[3] and David Grosso.*[1,2]

[1] Center for Interdisciplinary for Nanoscience of Marseille, CINaM, UMR 7325 Campus de Luminy – Case 913, 13288 Marseille, France.

[2] Solnil SAS, 95 rue de la république, 13002, Marseille, France (badre.kerzabi@solnil.com).

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Metal oxide (MO_X) nanopatterns have been prepared from Soft-Nano-Imprint-Lithography (soft-NIL) combined with sol-gel formulations. A careful adjustment of the chemical parameters and processing conditions are used to obtain faithful replicas with high vertical aspect ratios up to 3 and refractive index up to for instance 2.7@520 nm with TiO_2, on glass, silicon wafers or fused silica. This method is CMOS-compatible, cost-effective and easy to scale-up.

As-deposited metal oxides sol-gel layers are rather difficult to imprint as a result of the fast evaporation-induced condensation of the precursors into stiff metal oxide networks that prevents efficient mass transfer within the cavities of the soft mould. Nonetheless, by adjusting the processing conditions to the pure inorganic sol-gel chemistry we demonstrate that the process can be highly simplified while improving the quality of the replicas and avoiding the use of sacrificial, stabilising, organic agents that is always accompanied by a high shrinkage. A compromise can be found for all sol-gel materials to reduce the xerogel viscosity necessary for capillary filling, while limiting the shrinkage upon final thermal curing. Metasurfaces bearing arrays of high aspect-ratio 3D features of different shapes and composed of hard ceramics with controlled functionalities are directly available with such a one-step process. Besides, this method is compatible with high-throughput on 200 mm glass and silicon wafers (limited only by the machine in use) and conventional production constraints. It also benefits from the countless chemical compositions available from sol-gel chemistry and has been demonstrated with many metal oxides.

In this presentation, we will focus on Silica (SiO_2), Titania (TiO_2), Alumina (Al_2O_3), and Europium-doped Zirconia (ZrO_2:Eu^{3+}) as pristine, hybrid, or mesoporous materials. They have been patterned with different designs and bearing different motif dimension (down to 100 nm) and aspect ratio (up to 3), to address different functionalities such as controlled-wetting surfaces, light harvesting coatings, diffraction gratings for light extraction, multispectral filters, enhanced spectrally and spatially controlled emitting surfaces, wave guides, structural color coatings, anti-reflection coatings, photonic VOC sensors, or flow cells for DNA sequencing.

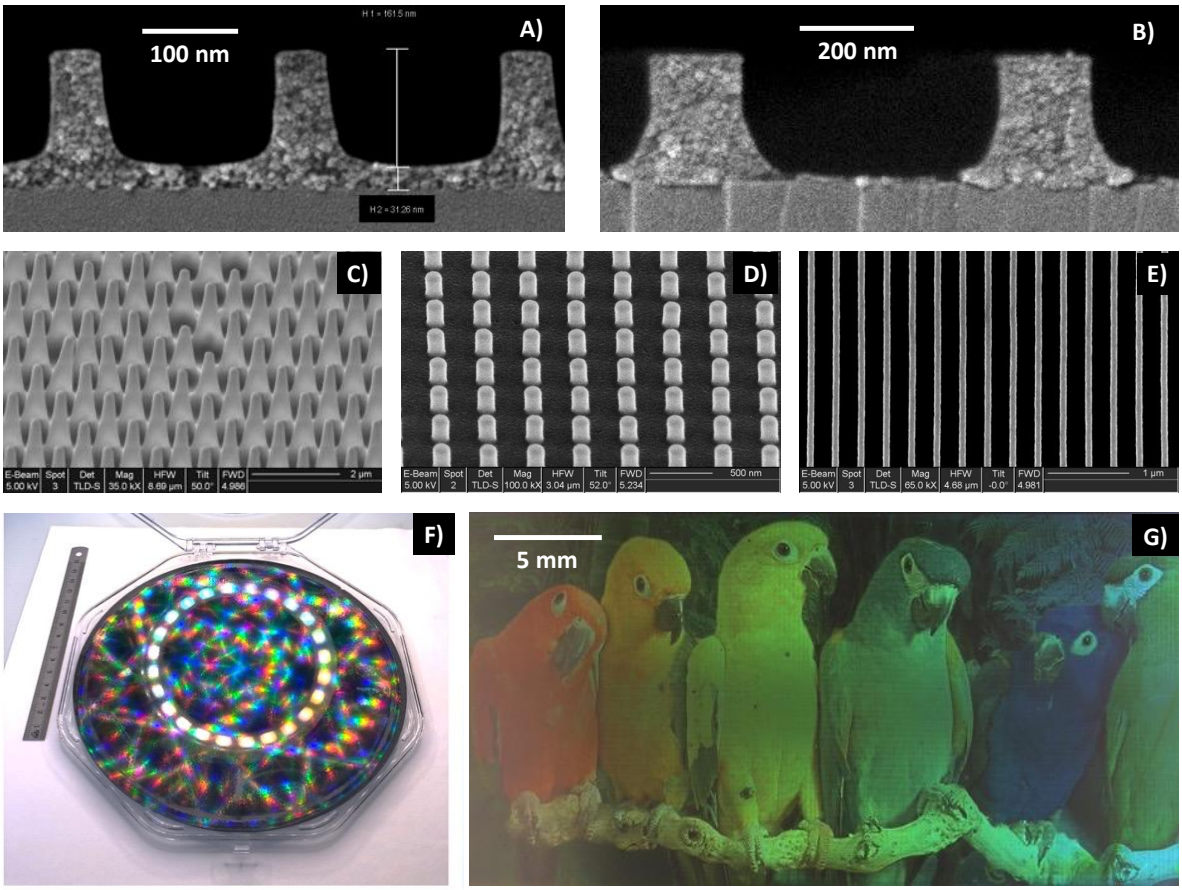

Figure 1 : SEM images of A) and B) TiO_2 (RI=2.56) motif profiles with and without residual layer ; C) SiO_2 elongated pyramids as anti-reflection coatings, D) Eu dopped ZrO_2 as photoluminescent resonators, E) TiO_2 (RI = 2.3) gratings for light coupling, F) image of a 200mm diameter wafer imprinted with SiO_2 using Obducat tool and G) image composed of structural color pixels imprinted in TiO_2 (RI = 2.2).

REFERENCES

1) Zeinab Chehadi, Michele Montanari, Nicoletta Granchi, Mehrnaz Modaresialam, Mathieu Koudia, Mathieu Abel, Magali Putero, David Grosso, Francesca Intonti, and Marco Abbarchi. Soft Nano-Imprint Lithography of Rare-Earth-Doped Light-Emitting Photonic Metasurface**, Advanced Optical Materials,** 10, 21, 2022, 2201618, DOI 10.1002/adom.202201618.
2) Modaresialam, M.; Bordelet, G.; Chehadi, Z.; O'Byrne, M.; Favre, L.; Putero, M.; Abbarchi, M.; Grosso, D. Enhanced Refractive Index Sensitivity through Combining a Sol-Gel Adsorbate with a TiO_2 Nanoimprinted Metasurface for Gas Sensing. 2021, **ACS Applied materials & interfaces**. DOI:10.1021/acsami.1c13248
3) M; Chehadi, Z; Bottein, T; Abbarchi,; Grosso, D. Nanoimprint Lithography Processing of Inorganic-Based Materials (review). Modaresialam, 2021, **Chemistry of Materials**. DOI: 10.1021/acs.chemmater.1c00693
4) Bochet-Modaresialam, Mehrnaz; Claude, Jean-Benoit ; Grosso, David ; Abbarchi, Marco. Methylated Silica Surfaces Having Tapered Nipple-Dimple Nanopillar Morphologies as Robust Broad-Angle and Broadband Antireflection Coatings. **ACS Appl. Mater. Inter. 2020**, 3, 5231-5239, DOI: 10.1021/acsanm.0c00646.
5) S. Checcucci, T. Bottein, M. Gurioli, L. Favre, D. Grosso, M. Abbarchi. Multifunctional metasurfaces based on direct nanoimprint of titania sol-gel coatings. **Adv. Opt. Mater.** 2019 7, 10, AN 1801406. DOI: 10.1002/adom.201801406
6) Faustini, Marco, Cattoni, Andrea, Peron, Jennifer, Boissiere, Cedric, Ebrard, Paul, Malchere, Annie, Steyer, Philippe, and Grosso, David.Dynamic Shaping of Femtoliter Dew Droplets. **ACS NANO**, 12, **2018**, 3243-3252. **DOI:** 10.1021/acsnano.7b07699

Aluminum metasurfaces with high quality factors and spectral tenability

***Pascal Cheng*[1], Stéphanie Lau-Truong[1], Sarra Gam-Derouich[1], Alexandre Chevillot-Biraud[1], Abderrahmane Belkhir[2], Macilia Braik[2], Claire Mangeney[3*] and Nordin Félidj[1*]**

[1] ITODYS, CNRS UMR 7086, Université Paris Cité, Paris, France , [2] LPCQ, Université Mouloud Mammeri, Tizi-Ouzou, Algeria, [3] LCBPT CNRS UMR 8601, Université Paris Cité, Paris, France

Aluminum, despite being less explored compared to widely used gold or silver nanoparticles (NPs) in the field of plasmonics, offers numerous advantages. This metal is characterized by a low cost and exhibits optical response governed by the excitation of localized surface plasmons, enabling coverage of a broad spectral range from UV to NIR. However, aluminum NPs suffer from poor quality factors, particularly in the visible range (Q ~ 2). These limitations arise due to inherent losses caused by electron damping, which result in a broad resonance and restrict their potential applications in detection and color filtering. For instance, detecting subtle changes in the surrounding medium, such as the addition of an analyte, becomes challenging when dealing with a broad resonance. On the other hand, achieving color filtering necessitates a narrow resonance to selectively filter a specific color rather than a wide range of colors.

The primary objective of this work is to obtain aluminum structures with high-quality factors. To accomplish this, we propose arranging the NPs in a regular pattern and taking into account strong long-range interactions, leading to the generation of a very narrow resonance known as surface lattice resonance. We successfully achieved remarkable and unprecedented values of Q (~ 60) in air, emphasizing the significance of substantial long-range interactions among the NPs.

Furthermore, aluminum NP arrays exhibits higher-order diffracted modes, which are much more pronounced compared to gold and silver. This is due to their lower absorption capacity. As a result, it provides the opportunity to generate a broader range of wavelengths in the visible range (in comparison to gold or silver). This can be displayed in a dispersion diagram (figure below), up to 3 surface lattice resonance can be observed for some grating constant (distance between each nanoparticle in the lattice) following different diffracted orders. The experiment fit is in good agreement with theoretical calculations by FDTD.

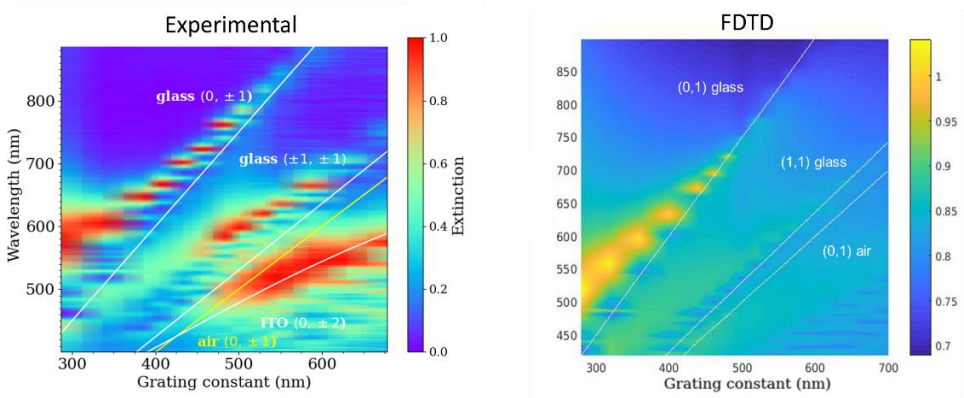

fig 1 : On the left experimental and on the right FDTD dispersion diagram for aluminum arrays

Reproducing the Fresnel-Arago experiment to illustrate physical optics - *Live Demo*

Jérôme Wenger [1]

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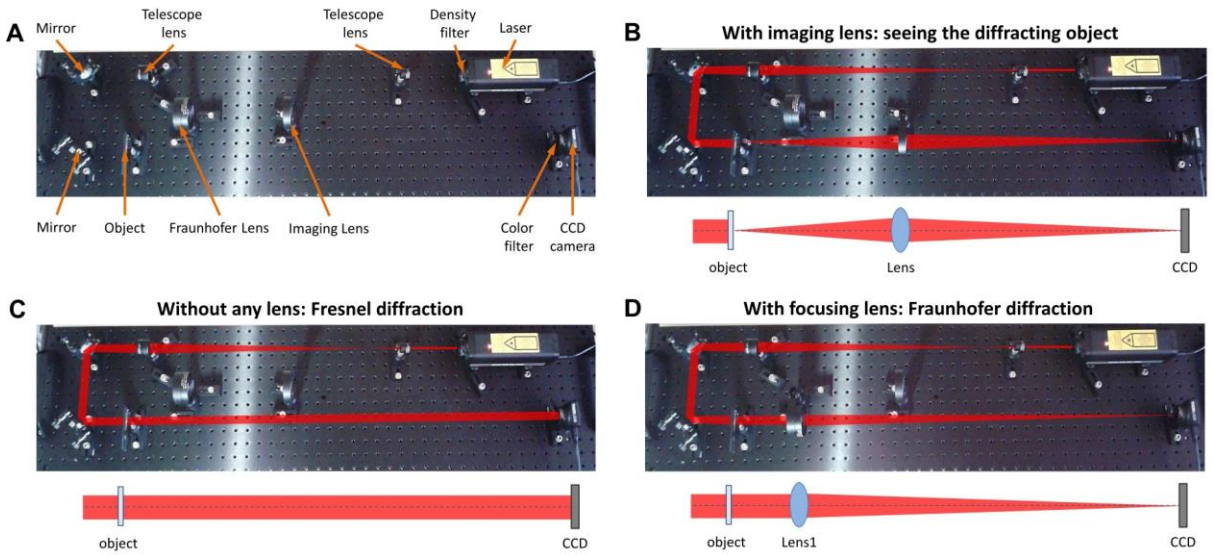
E-mail: jerome.wenger@fresnel.fr

Is there a bright spot in the shadow of an opaque disk? 200 years ago, Augustin Fresnel and François Arago's remarkable answer to this question validated the wave theory of light and inaugurated the modern theories of diffraction. Today, their renowned experiment can be easily reproduced using lasers and cameras. Far beyond its historical interest, the experiment is a versatile platform to illustrate the main concepts of optical physics, including diffraction, interference, speckle, and Fourier optics.



References

[1] Wenger, J., Rogez, B., Chaigne, T., & Stout, B. (2020). Reproducing the Fresnel-Arago experiment to illustrate physical optics. Photoniques, (104), 21-25.

[2] Rogez, B., Chaigne, T., & Wenger, J. (2020). Reproducing Fresnel-Arago historical experiment: a visual illustration of the main concepts of physical optics. arXiv preprint arXiv:2002.03743.

Role of optical rectification in photon-assisted tunneling current

P. Février, J. Basset, J. Estève, M. Aprili, J. Gabelli[1]

[1] *Laboratoire de Physique des Solides, CNRS, Univ. Paris-Sud, Université Paris-Saclay, 91405 Orsay, Cedex, France*

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Emission of light and conversely rectification of an optical signal using an all-metallic electronic device is of fundamental and technological importance for nano-optics. However, despite recent experimental efforts in the development of electrically driven plasmonic sources also related to progress to obtain highly confined optical modes, the interplay between quantum transport and optics is still under debate. Here, we measure the photon-assisted current in a planar tunnel junction under infrared illumination at λ=1.55 μm in the Kretschmann configuration (Fig 1). To address the microscopic mechanism at the origin of the optical rectification, we compare the photon assisted current and the current-voltage characteristics of the junction measured on a voltage range much greater than V_0=hν/e≅0.825 V, previously unexplored. The experimental results do not agree with the theory based on the existence of a non-thermal out-of-equilibrium distribution function in the electrodes and corresponding to the exchange of energy quanta between electrons and photons. We show instead that the illumination power mainly goes into heating and that the rectification results from the tunneling Seebeck effect.

References

[1] Février, P., Basset, J., Estève, J. *et al.* Role of optical rectification in photon-assisted tunneling current. *Commun Phys* **6**, 29 (2023)

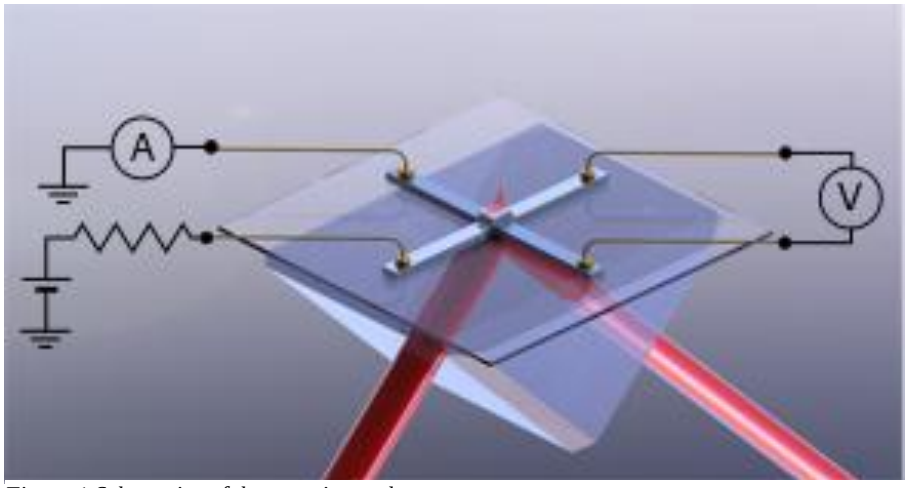

Figure 1.Schematics of the experimental setup

Plasmon-mediated photoelectrochemical transformations of tetrazine derivatives followed by Fluorescence microscopy coupled with Scanning Electrochemical Microscopy.

Ali Dabbous[1], Baptiste Maillot[1], Jean-Frédéric Audibert[1], Vitor Brasiliense[1] and Fabien Miomandre[1].

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Plasmonic nanoparticles exhibit unique optical properties characterized by the high extinction coefficient, the ability to support localized surface plasmon resonances (LSPR), and the generation of free electrons that can collectively oscillate in response to the incident light. Profiting from their properties, they attracted significant attention in various fields, including sensing, imaging, photothermal therapy, catalysis, and energy storage applications[1][2].

In this work, surfactant-free plasmonic gold nanoparticles (AuNPs) are electrodeposited on ITO plates. Then, tetrazine derivatives as redox-active luminescent probes are selected to study the plasmonic-induced photoelectrochemical processes. To investigate the activity of the possible hot carriers generated from the plasmon-excited AuNPs, a set-up consisting of a focalized laser irradiation and fluorescence microscope combined with scanning electrochemical microscopy (SECM) was employed[3].

Two tetrazine derivatives are used in this study, allowing the investigation of the redox processes either in solution or on the surface of the AuNPs through the grafted monolayers of a thioctic tetrazine derivative[4]. In both cases, we show the efficiency of the hot carriers generated from the plasmonic AuNPs to induce redox reactions with the tetrazine probes. Upon plasmonic excitation, a change in the electrochemical tip current is observed in the SECM measurements, accompanied by the quenching of the tetrazine's fluorescence (Fig. 1). The variation of the experimental parameters, such as the change of the applied tip potential, the irradiation laser power, and the alignment of the focalized laser with the SECM-UME Tip shows that the plasmonic activity is actually the dominant process in our systems.

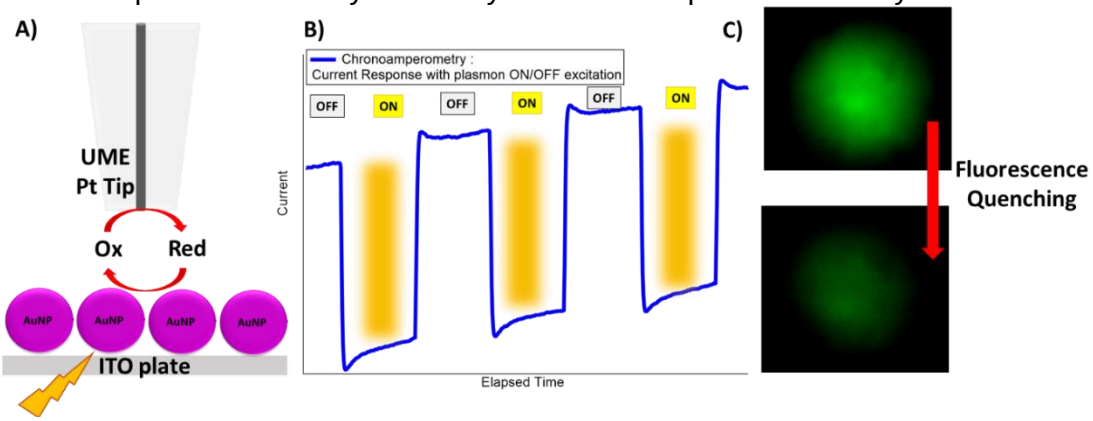

***Figure 1: Experimental Investigations**: A) Schematic representation of the SECM measurements on the AuNPs-ITO surface. B) The current response monitored during the laser switch ON/OFF. C) Fluorescence quenching of the tetrazine molecules recorded using the fluorescence microscope.*

References:

[1] J. Liu *et al.*, *Materials*, vol. 11, no. 10, Art. no. 10, 2018.
[2] Y. Yu, *et al*., *ACS Nano*, vol. 13, no. 3, pp. 3629–3637, 2019.
[3] L. Guerret-Legras, *et al*., *J. Phys. Chem. C*, vol. 124, no. 43, pp. 23938–23948, 2020.
[4] L. Oliveira de Miranda *et al.*, *J. Phys. Chem. C*, vol. 127, no. 7, pp. 3660–3670, 2023.

DNA nanotechnology as a playground for plasmonics

S. Bidault[1]

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Plasmonic resonators featuring high extinction cross sections, as well as strongly confined and enhanced optical fields, have found diverse applications by optimizing light-matter interactions but also by providing an optical contrast to chemical analytes in biosensing. Structural DNA nanotechnology provides numerous degrees of freedom to develop hybrid plasmonic resonators with a perfectly controlled chemical environment in order to optimize these optical properties. In this presentation, I will discuss two approaches that we have recently developed using DNA nanotechnology to maximize the interaction between quantum emitters and plasmonic resonators, as well as to detect single DNA single strands on a color camera thanks to plasmon coupling.

In particular, dimers of gold nanoparticles can be assembled on a simple DNA double-strand in order to introduce a controlled number of quantum emitters such as fluorescent molecules in plasmonic antennas with nanoscale precision. This allows the enhancement of spontaneous single photon emission by more than two orders of magnitude while maintaining high fluorescence quantum yields. The active reduction of interparticle spacings below 2 nm also allows a strong coupling regime to be reached between such plasmonic resonators and less than five resonant organic molecules, opening exciting perspectives to observe few-photon nonlinearities at room temperature [2,3].

Furthermore, I will detail how a hybrid nanostructure based on spherical gold particles and a dynamic DNA origami can detect single biochemical interactions by monitoring nanoscale conformation changes using near-field plasmon coupling. Single nanostructure scattering spectroscopy measurements can be correlated to a simple colorimetric detection scheme on a CCD camera. These measurements indicate that label-free single biomolecule sensing could be achieved in parallel on low-cost equipment.

References

[1] J. Heintz, N. Markesevic, E.Y. Gayet, N. Bonod, S. Bidault, ACS Nano 15, 14732 (2021)

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Ultraviolet Resonant Nanogap Antennas from Rhodium Nanocubes for Enhancing Protein Intrinsic fluorescence.

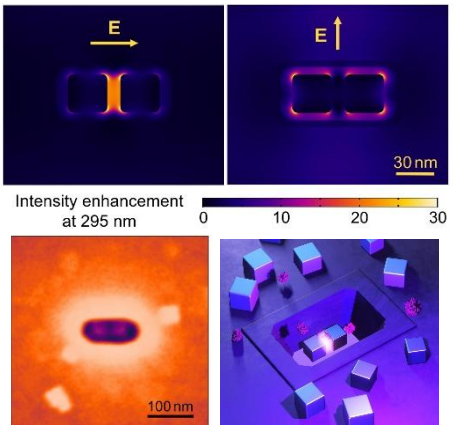
Prithu Roy,[1] Siyuan Zhu,[2] Jean-Benoît Claude,[1] Jie Liu,[2] Jérôme Wenger[1,*]

[1] *Aix Marseille Univ, CNRS, Centrale Marseille, Institut Fresnel, AMUTech, 13013 Marseille, France*

[2] *Department of Chemistry, Duke University, Durham, NC 27708, USA*

** Corresponding author: jerome.wenger@fresnel.fr*

Studying individual proteins in their untouched, native state—without the aid of fluorescent labels—is critical for obtaining a holistic understanding of their behaviors and roles in vivo. However, the traditional methods of fluorescence labeling often manipulate the structure and functionality of proteins, yielding inaccurate results. To counter this issue, our team has pioneered a ground-breaking, label-free detection platform that operates in the ultraviolet (UV) range for the examination of single proteins. This platform leverages the proteins' inherent UV autofluorescence and employs an innovative optical horn antenna design, offering unrivaled resolution and sensitivity.[1]



While the current technology represents the forefront of the field, it does exhibit limitations, such as a restricted enhancement of photon count rate—only 10-15 times higher than that of confocal methods [2]. To push beyond this boundary, we're investigating the potential of self-assembling rhodium cube gap antennas within a rectangular zero-mode waveguide, driven by capillary-convective forces. The results have revealed that the amplification of the excitation signal (at wavelengths of 266 and 295 nm) and the emission signal from tryptophan (at 350 nm) is two magnitudes higher than what is possible with confocal methods and a magnitude higher than the current cutting-edge techniques. Moreover, our experiments, conducted on self-assembled nanoantenna for detecting P-terphenyl dye molecules, streptavidin, and Hemoglobin, have consistently exhibited an enhancement in UV fluorescence within the nano-gap antenna—a finding that aligns with our numerical simulations.

References

[1] **Barulin, A., Roy, P., Claude, JB., Wenger,J.** "Ultraviolet optical horn antennas for label-free detection of single proteins". *Nat Commun* **13,** 1842 (2022).

[2] **Prithu Roy** et al "Ultraviolet Nanophotonics Enables Autofluorescence Correlation Spectroscopy on Label-Free Proteins with a Single Tryptophan" *Nano Lett.*(2023)

Observation of DNA strand interaction with SERS

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Surface-enhanced Raman spectroscopy has demonstrated its ability as powerful tool that can provide us information about the structure and the conformation of molecules such as DNA.

In this work, we used an Hamamatsu commercial SERS substrate [1], to study the interaction between a DNA sequence consisting of 20 Bases of poly-Thymin (PolyT) with its complementary poly-Adenin (PolyA) composed of 19 Adenin bases and one Cytosin in different positions throughout the polyA strand (1, 5, 10, 15 and 20) to create a mismatch. The PolyA strand is grafted at the surface of the gold nanostructured surface using a thiol group at the 5' extremity of the DNA strand. the SERS substrate is incubated in 450 µl of PolyA (10^{-4} M) in TE buffer for 15 hours. The surface is then washed to remove the PolyA excess. We assume that we form a monolayer of PolyA. Some solutions of PolyT with different concentrations (10^{-7}, 10^{-6}, 10^{-5} and 10^{-4} M) are successively deposited on the SERS substrate. We performed Raman mapping on the surface and we recorded 400 spectra using a 633 nm excitation wavelength. One can observe the 735 cm^{-1} band assigned to the ring breathing mode of the PolyA and some variations of its intensity depending on the position on the map. By changing the concentration, we observe a decrease of the average SERS intensity of this band as well as a decrease of the standard deviation of the intensity of this band. We interpret this intensity change by some modification of the orientation and flexibility of the PolyA DNA strands interacting with the PolyT [2]. The increase of the concentration of Poly-T induced a loss of flexibility of the PolyT/PolyA molecular complex. This study provides a new approach for the reliable quantification and structural analysis of biological molecules.

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Gap-plasmon crystallography

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Plasmonic nanocavities have the ability to confine light in extremely small volumes, enhancing the electromagnetic field and providing a highly sensitive and reproducible platform. Using plasmonic nanocrystals, this tunability is achieved by adjusting the nanoparticle size, the gap spacing, and the gap spacer refractive index. These phenomena are receiving increasing attention by the nanophotonics and nanoelectronics communities due to their potential applications in optoelectronics, quantum optics, and novel nanophotonic and plasmonic-circuit devices. In this study, we investigated gap plasmon resonators made of silver nanocubes separated from a]gold mirror by thin dielectric layers ($Al2O_3$, TiO_2). First, we studied the impact of dielectric thickness, refractive index and nanocube size on individual resonators, supported by correlative SEM microscopy. This enabled us to gain insights on the system sensitivity to various parameters. Next, we show that this platform can be used to assess the removal of residual capping ligands (such as PVP) on the nanocube surface, which hampers use in nanoelectronics applications. Finally, by performing polarisation-resolved measurements on birefringent anatase layers (2-10nm), we show that we can identify their crystal orientation with a sub-100nm spatial resolution, despite their extremely small thickness. We found a wide range of possible orientations and no specific epitaxial relationships with the underlying polycrystalline gold film. EBSD measurements on thicker anatase layers confirmed these findings. This work further extends the use of gap-plasmons to a new domain.

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Study of thermoplasmonic properties of AuNPs in visible and near infrared region

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Photothermal therapy (PTT) is a technique used for cancer treatment that exploits the thermoplasmonic properties of gold nanoparticles (AuNPs). In fact, AuNPs convert electromagnetic radiation into heat due to the excitation of the plasmon. Such property can be used for the thermal ablation of tumor cells. AuNPs of specific sizes and shapes are able to convert visible or near-IR radiation into heat [1]. The aim of this project is to study the thermoplasmonic properties of AuNPs in the visible to near-IR area, by observing and analyzing temperature variations. The first part of this study consists of synthesizing different shapes and sizes of AuNPs to exploit their physico-chemical properties. The AuNPs are characterised by UV-Visible to determine the position of the localized surface plasmon resonance (LSPR). In a second part, we focus on the the thermoplasmonic study of AuNPs alone and after functionalization with a PEG molecule. Using a thermal camera, we measure the temperature rise induced by laser excitation on colloidal solutions at different wavelengths. We determine the direct influence of several experimental conditions: size, shape and environment of the AuNPs, on the temperature variation.

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Heat Transfer inside Cross-shaped Nanoparticles

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By absorbing and converting light into heat, nanoparticles (NPs) behave as highly localized sources of heat. However, it is challenging to control thermal dynamic inside NPs due to the time and space scale involved in the photothermal process (femtosecond and nanometer scale). In this work, we predict with our numerical model[1] heat transfer inside cross-shaped gold nanoparticles and confirm it with femtosecond transient spectroscopy measurement. This NP geometry is known to support a polarization-dependent localized plasmonic resonance (LSPR) along each of its branches. By selectively exciting one LSPR, we can heat only the wished branch, then, the heat will propagate along the other branch. By measuring the temporal delay between the modulation of LSPR intensity of each branch, we put in evidence the thermal inhomogeneity inside the cross-shaped NP. Good agreement was found between simulations and experiments[2]. In addition, by fitting the experimental data with our model, we can extract the spatio-temporal electronic and lattice temperature dynamic inside the NP. An illustration of the experiment is shown in figure 1.a. The pump is used to heat one branch of the cross and the probe to measure optical change of both branches. Figure 1.b shows a simulation of the resulting electronic temperature (T_e) reached few femtoseconds after the excitation. We can see the asymmetric electronic temperature distribution inside the cross. Figure 1.c shows the measured optical response delay between the longitudinal and transverse LSPR.

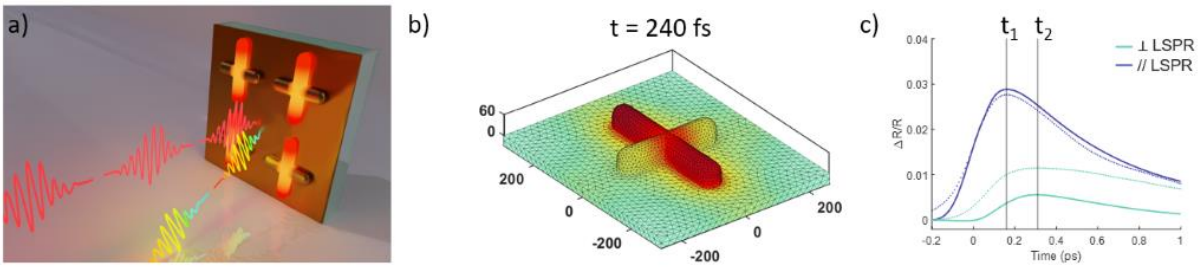

Figure 1: a) Concept of the experiment. b) Simulation of the repartition of T_e inside a nanocross at t = 240 fs. c) Experimental (dots) and modelized (continuous line) transient reflectivity at the resonance wavelength of each cross axes (the longitudinal in green and transverse in blue).

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Optimizing the synthesis of gold nanotriangles and evaluating their potential in LSPR sensing

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The synthesis of plasmonic nanoparticles has drawn great attention in the last decades. The study of crystal growth mechanisms and optimization of the existing techniques lead to the increasing accessibility of nanomaterials, which have a high potential in the fields of plasmonics and catalysis [1-6]. However, promising shape-anisotropic structures are not thermodynamically favorable and can be only derived following fine and laborious procedures the mechanisms of which have not been studied thoroughly yet [7-9]. We examined the existing seed-mediated synthesis of gold nanotriangles [10] with UV–VIS time-resolved measurements. Tracing the particle evolution allowed for defining the critical time points for each step and reducing the time consumption from three days to one only without a loss in final product quality [11]. Next, we develop the synthesis utilizing a continuous microfluidic setup, which provides a highly efficient mixing and simple parameter control [12]. We show that the crystallinity of primary seeds is determined by the type of the implemented reactor, which further influences the shape yield [13]. The use of microfluidic seeds leads to the formation of well-defined triangles with narrower size distribution compared to the entirely conventional batch synthesis. These studies allow us to design an automatized platform for micro-continuous flow synthesis. Together with thorough parameter optimization, it will bring a new potential in streamlining and scaling up nanomaterial production, which in turn would provide a cost reduction in sensor fabrication.

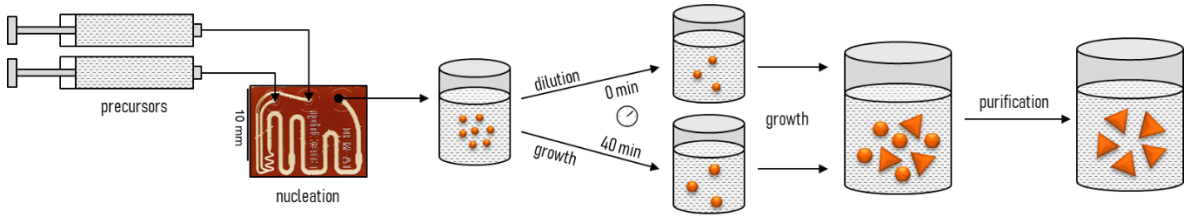

Figure 1. The representation of gold nanotriangle synthesis implementing a microfluidic setup

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The Presence of Uncoated Nanoparticle Aggregates Determine the Phase of Phosphatidylcholine Lipids as Evidenced by Vibrational Spectroscopies

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Abstract

Spherical structures built from uni- and multilamellar lipid bilayers (LUV and MLV) are nowadays considered not just as nanocarriers of various kinds of therapeutics, but also as the vehicles that, when coupled with gold (Au) nanoparticles (NPs), can also serve as a tool for imaging and discriminating healthy and diseased tissues. Since the presence of Au NPs or their aggregates may affect the properties of the drug delivery vehicle, we investigated how the shape and position of Au NP aggregates adsorbed on the surface of MLV affect the arrangement and conformation of lipid molecules. By preparing MLVs constituted from 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC) in the presence of uncoated Au NP aggregates found i) both within liposome core and on the surface of outer lipid bilayer, or ii) adsorbed on the outer lipid bilayer surface only, we demonstrated the maintenance of lipid bilayer integrity by microscopic techniques (cryo-EM, TEM and AFM). The employment of SERS and FTIR-ATR tehniques enabled us not only to elucidate the lipid interaction pattern and their orientation in regards to Au NP aggregates, but also unequivocally confirmed the impact of Au NP aggregates on persistence/breaking of van der Waals interactions between hydrocarbon chains of DPPC.

Keywords:

1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC); Gold nanoparticle (Au NP) aggregates; interaction pattern and lipid phase change; microscopy (cryo-EM, TEM, AFM), spectroscopy (SERS and FTIR-ATR) and calorimetry

Surface Lattice modes for biosensing

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Confining the light at the metal nanostructures (NSs) scale is at the origin of many applications in nano-optics, molecular sensing, or surface enhanced spectroscopies. An important parameter in terms of LSP spectral features is related to the electromagnetic interaction between the NSs. For instance, the design of dimers of gold disks results in a significant red-shift of the LSP mode. At the opposite, strong electromagnetic long-range interaction can also occur, provided that the NSs are assembled in regular arrays. In such arrays, the optical properties are governed by the excitation of collective surface plasmon resonances, so-called Surface Lattices (SL) resonances. These SL modes raise from coherent scattering within the array, due to the periodicity of the NSs array, and stimulate a growing interest since a few years, as they offer unprecedented opportunities to tune the optical properties, with high quality factors (QFs).

Up to now, there is no detailed studies carrying out such sensitivity to the surrounding medium using SL modes. In this work, we demonstrate the crucial role of the grating constant on the sensitivity to the surrounding medium of plasmonic lattice surface resonances. In order to highlight this strong dependence, we exploit the diffraction coupling on square arrays of gold disks, deposited on an indium tin oxide layer on a glass substrate. In this work, we probed the sensitivity of various arrays to the surrounding medium, by measuring their extinction spectra (with grating constants varying from 250 to 500 nm), in distinct media. It is shown that the lattice surface resonances are strongly affected by the surrounding medium. Our experimental results are in very good agreement with the ones calculated by the finite-difference time-domain (FDTD) method, and highlight the crucial importance of the design of plasmonic devices displaying strong long-range interactions in the context of molecular sensing.

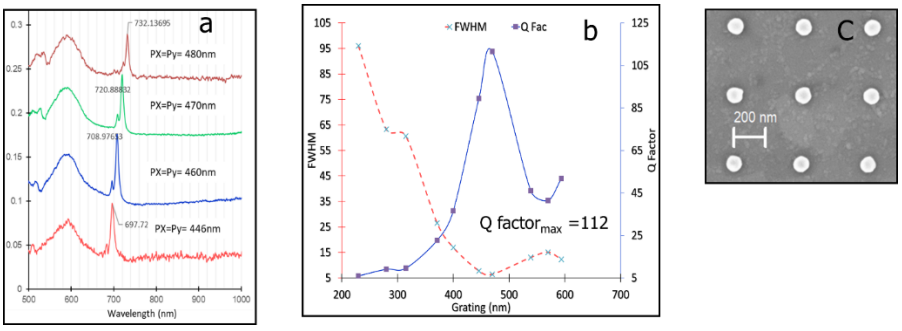

Figure: a) Extension spectra of the 2D regular array with a diameter of 100nm and interparticle distances of 446nm, 460nm, 470nm, and 480nm. b) Plot showing the relationship between Full Width at Half Maximum (FWHM), Quality Factor, and grating pitch for the 2D regular array with a diameter of 100nm. c) Scanning Electron Microscopy (SEM) image of the 2D regular array with a diameter= 100nm

FDTD calculations: a crucial tool to predict and interpret LSPR experimental results

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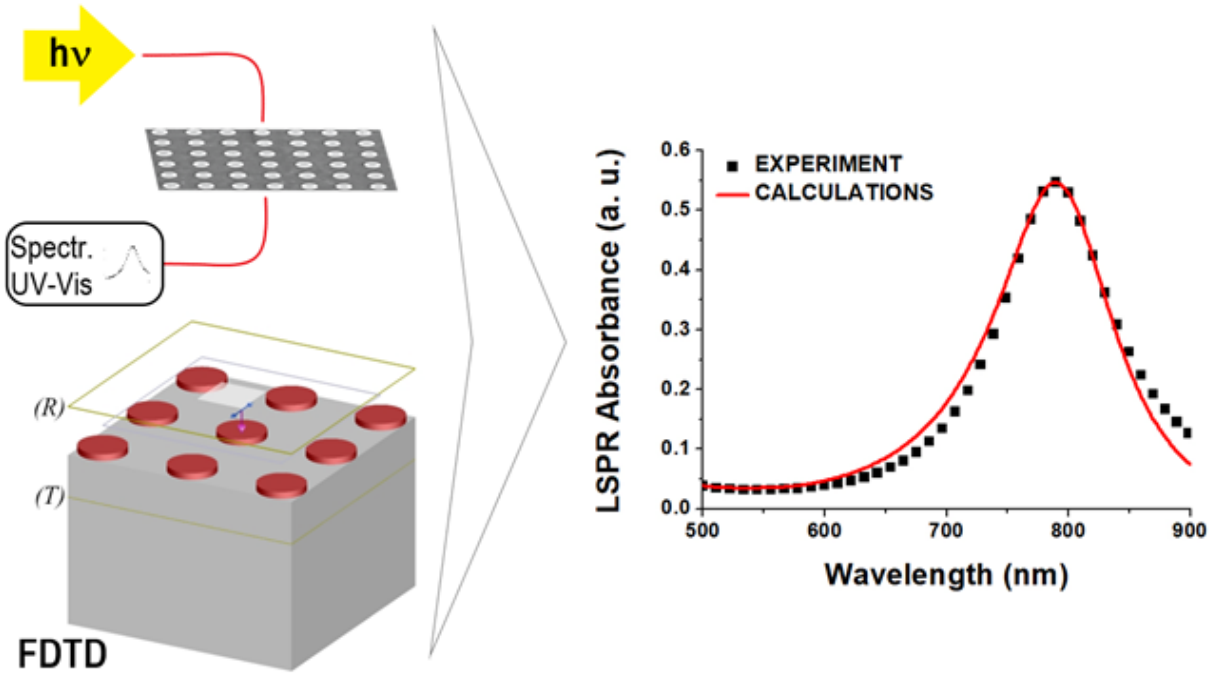
FDTD simulations enable us to predict the physical parameters of nanostructures, which will theoretically give the best experimental LSPR signals. This information is crucial to optimize sample fabrication and to avoid wasting a lot of time and money.

Simulation is also essential for controlling and calibrating the various parameters of fabricated nanostructures, and for understanding certain modifications to the samples, such as adding of Cr or ITO adhesion layers, covering nanostructures with dielectric layers, or thermal annealing...

Finally, FDTD calculations are helpful for interpreting LSPR experiments and better understanding the adsorption of gas molecules on Au LSPR nanosensors and the catalysis of chemical reactions.



Polymère à empreinte moléculaire sur des surfaces plasmoniques

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Les toutes dernières années ont été marquées par des avancées importantes dans le domaine des polymères dits « à empreintes moléculaires » (Molecularly Imprinted Polymers - MIPs),[1] [2] Ces matériaux robustes sont capables de capter sélectivement un type de molécule donnée. Dans ce travail nous proposons une nouvelle stratégie pour construire un capteur facile à manipuler, stable et sensible cette strategie est basée sur le greffrage des MIPs sur des surfaces nanostructurées presentant des resonances plasmonique localisée (LSPR) et d'utiliser ce système hybride comme un capteur original LSPR/MIP ou SERS/MIPs. La position de la bande plasmon est tres sensible à l'environnement chimique et le SERS (surface-enhanced Raman scattering SERS) offre une grande sensibilité pour la détection de molécules à l'état de traces, tandis que les MIP offrent une plateforme de reconnaissance hautement sélective et spécifique. Pour préparer ces MIPs nous avons utilisé des monomères pi-conjugués comme momomères fonctionnels qui, par electrooxydation[3] ou electroreduction,[4] donnent des oligomères ou despolymeres conducteurs Ces polymères ont été synthethisés en presence des molecules d'interets environementals ou medicals comme cibles. Differentes combinaisions ont été etudiées: poly(3,4-éthylènedioxythiophène) / Carbamazépine (*EDOT/CBZ*), oligo(bisthienylbenzene/ Dopamine, (*BTB/DP*) et Aniline / dopamine *(Ani/DP)* . Pour carateriser et etudier la sensibilité et la specificité des MIP, nous avons utilisé le SERS , l'UV visible ainsi le shift (un déplacement) de la bande plasmonique. L'ensemble de ces resultats seront présentées.

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Spatially-Localized Functionalization on Nanostructured Surfaces for Enhanced Plasmonic Sensing Efficacy

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Plasmonic gold nanostructures are being used to develop high-performance biosensors. The confinement of electromagnetic fields far beyond the diffraction limit has led to single-molecule detection through surface-enhanced Raman spectroscopy (SERS). Tip-Enhanced Raman Spectroscopy (TERS) characterization, which has emerged as a powerful analytical technique providing high chemical sensitivity for surface molecular mapping with nanoscale spatial resolution, can provide nano-spatially resolved response and help in designing highly sensitive and high-resolution biosensing structures. This work examined the TERS performance of functionalized gold nanodisk arrays on a gold-coated glass substrate. These samples have shown results in SERS [1] upon coupled plasmonic modes: the gold layer sustains propagative surface plasmons while the nanostructures sustain localized surface plasmon resonances. Nano-resolved TERS response distribution from grafted thiophenol molecules on nanodisks of 110 and 220 nm diameter feature strong signal localization on the periphery of the nanostructures, in agreement with numerical modeling [2]. This highlights the importance of grafting molecules on high electric field locations to optimize detection sensitivity and speed at low molecular concentrations.

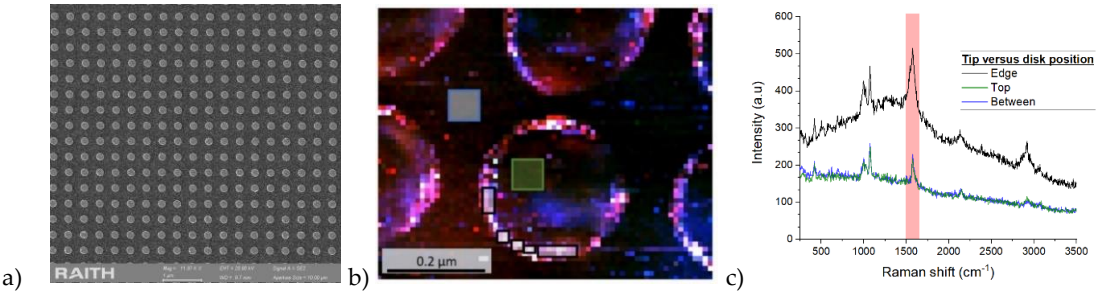

Fig. 1 a) SEM picture of gold nanodisk arrays (220nm diameters, 400nm periods). b) TERS mapping with a 638 nm laser. In the TERS image, the pixel size is 10×10 nm². c) Raman signal for three identified regions of the sample: Top – Edge – Between.

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Fabrication of plasmonic metasurfaces for fluorescence nanoscopy

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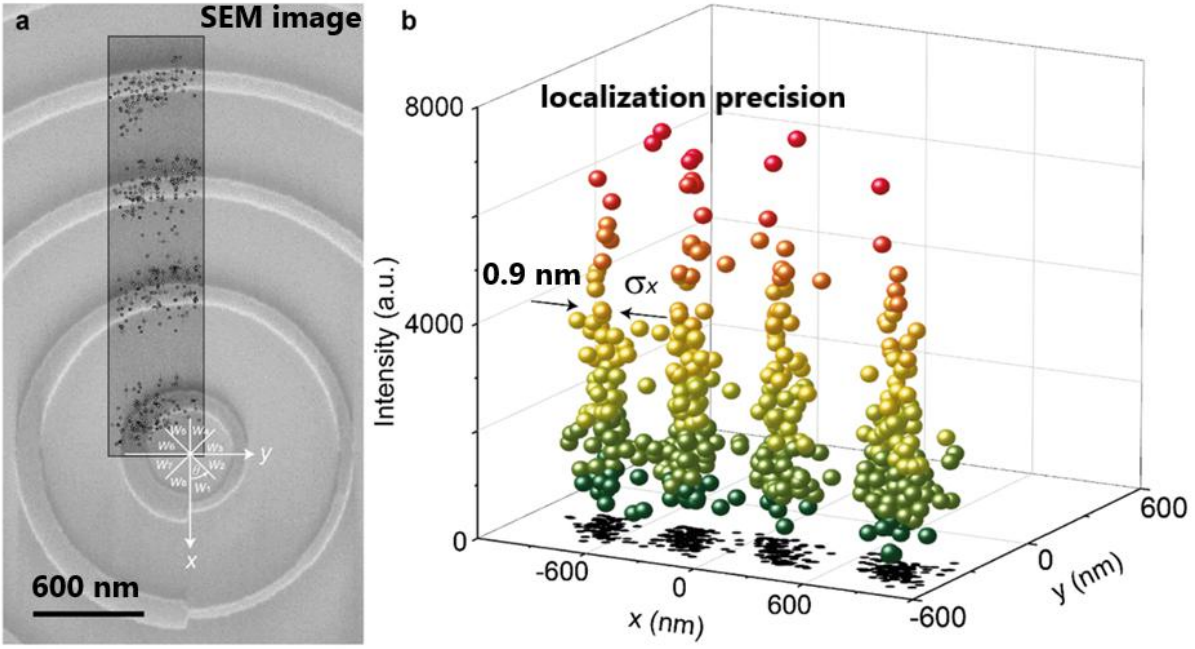
Single-molecule fluorescence localization microscopy has become an indispensable technique of imaging with resolution better than 10 nanometers. However, the light emission of fluorophores is not easy to control because of photobleaching. In the presence of nanoantennas, the photobleaching lifetime, blinking rate and overall photoluminescence intensity can be strongly increased due to the Purcell effect.
We fabricated arrays of plasmonic nanoantennas organized as cyclic group metasurfaces coated with a fluorescent film for super-resolution imaging. Following a systematic study of fluorescence engineering using metamaterial-assisted localization microscopy (MALM), we show that improving the photostability of fluorophores and increasing the photoluminescence intensity in MALM enables imaging resolution with a localization accuracy of 0.9 nm.



Go beyond the limitations for trapping objects from micro to nanosize

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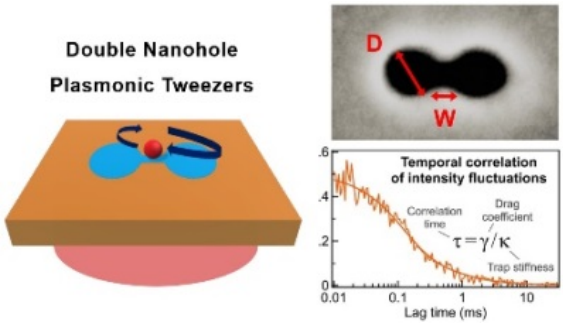
Immobilizing and manipulating small objects in the solution from the micron size to the nanoscale is always of interest for biologists, chemists as well as physicists. To realize it, plasmonic nanostructures have been introduced into the commercial optical tweezer module named **plasmonic nano-optical tweezers** (**PNTs**). PNTs as an upgraded version of conventional optical tweezers (Nobel Prize of 2018) go beyond the diffraction limitation to directly trap the nanosized objects under the high local intensity enhancement close to the nanostructures [1-3].

Since many factors influence this precise nano-manipulation, a very stable trapping system including an infrared trapping laser, a plasmonic nanoaperture and a fluorescence detection module is highly demanded. It allows to quantify various parameters such as trap stiffness, local temperature while trapping nano-objects. First, we introduce a method to measure the local temperature increase in the trap due to the trapping laser [4]. Second, we manage to take advantage of this plasmonic thermal effect to generate a large-scale thermophoretic force to assist the optical gradient force [5]. At the end, a method based on the correlation of fluorescence fluctuation of a trapped object has been developed for the trap stiffness quantification [6].



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Improving single molecule fluorescence detection with zero-mode waveguide nanoapertures

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Zero-mode waveguides (ZMW) are nanoapertures milled in opaque metal films with subwavelength diameters. Thanks to their strong light confinement, ZMWs have been reported to enable single molecule detection in concentrated solutions of several micromolars with enhanced fluorescence brightness. In this talk, I will describe recent applications of the ZMW concept:

The local temperature inside the ZMW can be accurately controlled by an infrared laser beam. The easy control of the temperature inside ZMWs opens their use for thermoplasmonics in confined sub-femtoliter volumes for nucleation, polymerization or crystal growth applications.

ZMWs can extend the spatial range of FRET to distances where dipole-dipole interactions would otherwise be too weak to produce detectable FRET signals. Using optimized structures a 3x FRET efficiency increase is observed at a large donor-acceptor distance of 13.6 nm, well beyond the classical Förster radius.

In the ultraviolet, ZMWs are used to monitor the autofluorescence of single label-free proteins with increased brightness, microsecond transit times and operation at micromolar concentrations. Working in the UV range is appealing to take advantage of the tryptophan fluorescence naturally present in proteins and rule out all the issues related external fluorescence labelling.

References

[1] Levene, M. J.; Korlach, J.; Turner, S. W.; Foquet, M.; Craighead, H. G.; Webb, W. W. Zero-Mode Waveguides for Single-Molecule Analysis at High Concentrations. Science 2003, 299, 682–686.

[2] Punj, D.; Ghenuche, P.; Moparthi, S. B.; Torres, J. de; Grigoriev, V.; Rigneault, H.; Wenger, J. Plasmonic Antennas and Zero-Mode Waveguides to Enhance Single Molecule Fluorescence Detection and Fluorescence Correlation Spectroscopy toward Physiological Concentrations. Wiley Interdiscip. Rev. Nanomed. Nanobiotechnol. 2014, 6, 268–282.

[3] Jiang, Q.; Rogez, B.; Claude, J.-B.; Baffou, G.; Wenger, J. Temperature Measurement in Plasmonic Nanoapertures Used for Optical Trapping, ACS Photonics 2019, 6, 1763-1773.

[4] Baibakov, M.; Patra, S.; Claude, J.-B.; Moreau, A.; Lumeau, J.; Wenger, J. Extending Single-Molecule Förster Resonance Energy Transfer (FRET) Range beyond 10 Nanometers in Zero-Mode Waveguides. ACS Nano 2019, 13, 8469–8480.

[5] A. Barulin, J.-B. Claude, S. Patra, N. Bonod, J. Wenger, Deep Ultraviolet Plasmonic Enhancement of Single Protein Autofluorescence in Zero-Mode Waveguides, Nano Lett. 19, 7434-7442 (2019).

Scientific days of the Active Plasmonics GDR - Marseille July 10-12th

Day 1 Monday July 10th

14:45 *Registration desk opening*

15:30 Welcome introduction words by GDR

15:35 Organization and logistics - Jérome Wenger

15:40 **Plenary: Beniamino Sciacca, CINaM**
Bottom-up plasmonic metasurfaces à la carte

16:15 **Wajdi Chaabani**, ITODYS, Paris
Self-Assembly of Anisotropic Plasmonic Nanoparticles in Confinement

16:35 **David Grosso**, CINaM, Marseille
Direct NIL patterning of sol-gel based metal oxides, with controlled refractive index from 1.2 to 2.7; applications in optics, photonics, and sensing

16:55 **Pascal Cheng**, ITODYS, Paris
Aluminum metasurfaces with high quality factors and spectral tunability

17:15 *Short Break*

17:30 **AfterConf event #1**
Fresnel-Arago experiment live demo

18:00 *End*

Day 2 Tuesday July 11th

8:45 *Registration desk opening*

9:15 **Plenary: Eric LeMoal, ISMO, Paris Saclay**
Plasmonics and nanophotonics with inelastic tunneling electrons

9:50 **Julien Gabelli**, LPS, Orsay
Role of optical rectification in photon-assisted tunneling current

10:10 **Ali Dabbous**, PPSM, Gif sur Yvette
Plasmon-mediated photoelectrochemical transformations of tetrazine derivatives followed by Fluorescence microscopy coupled with SEM

10:30 *Coffee Break*

11:05 **Sebastien Bidault**, Institut Langevin, Paris
DNA nanotechnology as a playground for plasmonics

11:25 **Prithu Roy**, Institut Fresnel, Marseille
Ultraviolet Resonant Nanogap Antennas from Rhodium Nanocubes for Enhancing Protein Intrinsic fluorescence

11:45 **Aicha Azziz**, IMMM, Le Mans
Observation of DNA strand interaction with SERS

12:05 **Peeranuch Poungsripong**, CINaM, Marseille
Gap-plasmon crystallography

12:25 *Lunch break*

13:30 **AfterConf event #2 Round table discussion: soft skills in and outside science**

14:00 *Mini break restart*

14:10 **Plenary: Guillaume Baffou, Institut Fresnel**
Optical wavefront microscopy in nanophotonics and thermoplasmonics

14:45 **Celia Arib**, IMMM, Le Mans
Study of thermoplasmonic properties of AuNPs in visible and near infrared region

15:05 **Jean-François Bryche**, LN2, Sherbrooke
Heat Transfer inside Cross-shaped Nanoparticles

15:25 *Coffee Break*

16:00 **Ekaterina Podlesnaia**, IPHT, Jena
Optimizing the synthesis of gold nanotriangles and evaluating their potential in LSPR sensing

16:20 **Qiqian Liu**, IMMM, Le Mans
The Presence of Uncoated Nanoparticle Aggregates Determine the Phase of Phosphatidylcholine Lipids as Evidenced by Vibrational Spectroscopies

16:40 **Kartikey Pandey**, ITODYS, Paris
Surface Lattice modes for biosensing

17:00 **Benjamin Demirdjian**, CINaM, Marseille
FDTD calculations: a crucial tool to predict and interpret LSPR experimental results

17:20 *Short Break*

17:35 **AfterConf event #3 Effective communication for scientists: tips & tricks**

18:20 *End*

Day 3 Wednesday July 12th

9:15 **Plenary: Anne-Laure Baudrion, UTT, Troyes**
Nonlinear optical sensing in arrays of plasmonic nanoparticles

9:50 **Sarra Gam**, ITODYS, Paris
Molecular Imprinted polymer on plasmonic surfaces

10:10 **Jean-François Bryche**, LN2, Sherbrooke
Spatially-Localized Functionalization on Nanostructured Surfaces for Enhanced Plasmonic Sensing Efficacy

10:30 *Coffee Break*

11:05 **Igor Ozerov**, CINaM, Marseille
Fabrication of plasmonic metasurfaces for fluorescence nanoscopy

11:25 **Quanbo Jiang**, UTT, Troyes
Go beyond the limitations for trapping objects from micro to nanosize

11:45 **Jerome Wenger**, Institut Fresnel, Marseille
Improving single molecule fluorescence detection with zero-mode waveguides

12:05 **Scientific round table discussion:**
perspectives for active plasmonics

12:35 Concluding words by GdR

12:40 *End*